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Rayleigh scattering and form factors

S C Roy[1], B Zhou[2], Lynn Kissel[3] and R H Pratt[4]

Department of Physics, Bose Institute, Calcutta-700 009, India

Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

Computations Physics Group, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260, USA

Abstract : A simple but useful approach, which has been widely used in estimating Rayleigh scattering cross sections, is the form factor (FF) approximation or its improved version, the modified form factor (MFF) approximations and as expected, this deviates substantially for photon energies near and below the photoeffect thresholds as well as for heavy elements and large momentum transfers. To remedy this failure of FF or MFF, anomalous scattering factors (ASF) defined as the deviation of the exact forward scattering amplitude obtained from FF or MFF, are often introduced. The dispersion relation between the real and imaginary parts of the forward scattering amplitude and the optical theorem relating the imaginary part to the photoabsorption cross section have been utilized to obtain the ASF Usually only bound-free photon absorption cross sections are used in calculating ASF. Complete calculation should include bound-bound transitions and bound pair production. ASF calculated considering the above contributions when used in combination with the FF or MFF, produces good result. Validity of different form factors comparing with present state-of-the-art exact S-matrix calculations and importance of ASF in calculating the Rayleigh scattering cross sections will be demonstrated.

Keywords : Rayleigh scattering form factors, anomalous scattering factors (ASF)

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1. Introduction

Rayleigh scattering by which we mean elastic scattering of photons (in the regime of X-rays and γ-rays) by bound atomic electrons. Elastic scattering, being one of the fundamental modes of interaction of photons, is a subject of investigation by its own right but its application to different fields, makes it of enhanced interest. Elastic scattering of x- and γ-rays from atoms, molecules and solids is important in obtaining informations on the inner structure of atoms and macromolecules [1], in medical diagnostics and imaging [2], in shielding calculations etc. Moreover, with the availability of synchrotron sources, new experimental information are emerging in the x-ray region and consequently the demand for accurate theoretical prediction of elastic scattering from bound atomic electrons is increasing.

An isolated atom consists of nucleus and bound electrons. Therefore, it is justifiable to consider the elastic scattering of photons by an atom as a coherent sum of contributions from the nucleus (nuclear Thomson scattering, nuclear resonance scattering), the bound electrons and contributions from quantum electrostatics (QED) effects (*e.g.* Delbruck scattering). At low photon energies, Rayleigh scattering (scattering off bound electrons) is predominant. Nuclear Thomson scattering is important with increasing atomic number (Z) of the target and is relatively important compared to Rayleigh scattering at large angle of scattering and photon energy. QED effects become important at higher photon energies.

Most calculations of Rayleigh scattering starts with describing the atom by a potential obtained in the framework of an independent particle approximation (IPA). In IPA, all atomic electrons move independently in a central potential due to the nucleus and the average effect of other electrons. IPA which neglects electron correlation is inadequate at very low photon energies (as in the optical range) and for light Z elements where electron correlations are important. However, as observed by Lin *et al* [3] for Helium ($Z = 2$), where the effects are observed to be largest, for total cross sections the effects are found to be < 10% by 100 eV, < 5% by 200 eV and < 1% by 400 eV. Correlation effect as observed by Ice *et al* [4] in scattering experiment of 5 and 12 keV photons from hydrogen and helium was later suspected when more accurate theoretical predictions were used [5]. Correlation effects, are expected to be small in the major regimes of photon energies ($\geq$ keV) of this article.

Up to now, the best available calculation to obtain Rayleigh scattering amplitudes was developed by Kissel *et al* [6] using the second order S-matrix. No systematic disagreement with its predictions have been noticed when compared with experimental results for a wide range of photon energies [7]. But this numerical method requires a considerable computation time especially for heavy atoms (due to large number of electronic subshells) and for high photon energies (due to the requirement of large number of multipoles to be considered), preventing its use for an extensive tabulation of scattering cross sections.

Most commonly used simple but approximate method in estimating the Rayleigh scattering cross sections, is the form factor (FF) approximation or its improved version, the modified form factor (MFF). As this requires less amount of computation time, extensive tabulations of FF and MFF are available for the elements $1 \leq Z \leq 100$ in the periodic table [8–10]. Both FF and MFF are small momentum transfer, high energy approximations and one expects substantial deviation at low photon energies, heavy elements and at large momentum transfer. Indeed form factors are found to fail at photon energies near and below photoeffect threshold, large momentum transfers and with increasing Z. MFF, in which the electron binding was included, produces better results for heavy elements and more importantly, gives the correct high energy limit in the forward direction.

To remedy the failure of FF and MFF at low photon energies, anomalous scattering factors (ASF), defined as the deviation of the exact forward scattering amplitude from FF or MFF, are often included. ASF has been obtained ultilizing the dispersion relation between the

real and imaginary parts of the forward scattering amplitude and the optical theorem relating the imaginary part to the photo absorption cross section. Usually phtoelectric cross sections are used as photo absorption cross sections thereby neglecting the bound-bound cross sections. It has been observed that more complete calculation including the bound-bound effects substantially improves the values especially for light elements and for ions.

We, in this present paper, intend to exhibit how FF or MFF can be used in conjunction with correctly computed ASF to obtain Rayleigh scattering cross sections comparable with the S-matrix predicted results. General validity of form factors, ASF and limitations of S-matrix calculations will also be discussed. To ensure effective comparison, all calculations (including FF, MFF, ASF) have been performed using the same atomic potential.

2. S-matrix calculations

The S-matrix is an operator which connects the final state of a time-dependent system with that of the initial state. For Rayleigh scattering, the matrix element $S_{fi} = \langle f|S|i\rangle$ represents the amplitude of a specific stationary state $\langle f|$ that evolved through scattering from the initial state $|i\rangle$. In IPA, the amplitude for scattering (S_{fi}) off each atomic electron should be calculated separately. Numerical methods to calculate Rayleigh scattering amplitudes by this way was first developed by Brown and his group. The calculation starts with the Feynman-Dyson representation of scattering in second order as shown in Figure 1. The effect of

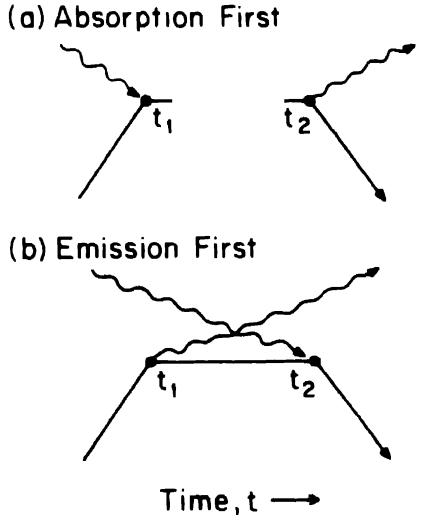


Figure 1. Feynmann diagram for lowest order contribution to the Rayleigh scattering amplitude · (a) "absorption first" contribution, (b) the "emission first" contribution.

binding in the intermediate state (times between t_1 and t_2) is important, which has been neglected in the form factor approximation. This calculation was later extended with the availability of faster computers. The present state-of-the-art 'exact' calculation is available due

to the pioneering work of Kissel *et al* [6]. Tabulated values of Rayleigh scattering cross sections [7] are available for 10 elements in the range of $13 \leq Z \leq 103$ and seven selected photon energies of experimentalists' choice in 65 angular steps in the range $0 \leq \theta \leq 180$. It is to be realized in this connection that the S-matrix calculation needs increasing number of multipoles to converge for a given subshell of electrons as the photon energy increases. The number of photon multipoles to be included increases as the ratio of incident photon energy to binding energy of the subshell electron increases. Therefore, it is often found to be impractical to calculate Rayleigh scattering amplitudes for all electrons using S-matrix, particularly for high Z atoms and for high photon energies. The usual procedure is to calculate the amplitudes exactly using S-matrix for those electrons for which the scattering contribution is significant and contributions from the rest of the electrons by using simpler approach. MFF is used to calculate the outer shell contributions with precision, since in most cases incident photon energy is very high compared to the binding energy of the outer shell and due to its capability of producing correct high energy limit amplitude. For photon energies below the K-threshold, either scattering contributions from all electrons to be computed using S-matrix or MFF may be used with anomalous corrections included.

As understood from Figure 1, calculation of accurate Rayleigh scattering amplitudes must include binding effects, in the initial, final and intermediate states. The numerical partial wave calculations include the binding effects in these states exactly to all orders in the IPA potential and hence are often referred to as exact calculation. One may argue that the calculation is performed in the lowest non-vanishing order in the S-matrix expansion, electron correlation was neglected and therefore is far from exact. It has been found that higher order expansion and correlation effects are not very important in the region of photon energies of this article. It is to be noted in this connection that the scattering amplitude calculated this way is accurate within 1% (best available at this time).

3. Form factors

Historically, form factor was developed as correction factor to the well known Thomson formula for scattering off a classical point electronic charge by an extended charge distribution. In other words, we can interpret the atomic form factor as characterising the effective charge that scatters the photon. The atomic form factor is defined as

$$f(q) = 4\pi \int \rho(r) \sin(qr)\, r^2 dr, \tag{1}$$

where $\rho(r)$ is the electron number distribution of the atom (assumed spherically symmetric and normalized to Z) and

$$hq = 2\,\frac{h\omega}{c}\,\sin\left(\frac{\theta}{2}\right) \tag{2}$$

is the momentum transferred to the atom as the photon is scattered through an angle θ. The scattering cross section in form factor is

$$d\sigma/d\Omega = \left(d\sigma_T/d\Omega\right) |f(q)|^2. \tag{3}$$

Here $d\sigma_T/d\Omega$ is the Thomson cross section derived considering the electron as a classical point charge, which for unpolarized photons is given by

$$d\sigma_T/d\Omega = \frac{1}{2} r_0^2 \left(1 + \cos^2 \theta\right). \tag{4}$$

The atomic form factor may be obtained from eq. (1) by using the $\rho(r)$ derived from the atomic ground state wavefunctions given by

$$\rho(r) = \sum_{n=1}^{\mathcal{L}} |\psi_n(r)|^2 = \sum^{\mathcal{L}} \rho_n(r) \tag{5}$$

where ψ_n is a single electron wavefunction. When relativistic bound state wavefunctions are used to derive the charge density and subsequently the form factor, the form factor thus derived is called the relativistic form factor. Although it has been demonstrated [11,12] that it is no service to include relativity in calculating charge distribution unless other competing processes are included at the same time.

Form factor with electron binding corrections are commonly known as modified form factor (MFF) and is represented by $g(q)$ instead of $f(q)$. The MFF for a given electron is given by

$$g(q) = 4\pi \int \rho(r) \frac{\sin(qr)}{qr} \frac{mc^2}{E - V(r)}, \tag{6}$$

where E is the total energy of the i-th electron ($E = mc^2 - \epsilon_i$, binding energy of the i-th electron), $V(r)$ is the atomic potential and $\rho(r)$ is the charge distribution associated with the i-th electron. Unlike $f(q)$, due to the presence of the term ϵ_i, $g(q)$ can not be calculated directly from the total charge distribution, instead contributions from each subshell should be taken into account separately. The corresponding cross section for unpolarised photons is given by

$$d\sigma/d\Omega = \frac{1}{2} r_o^2 \left(1 + \cos^2 \theta\right) |g(q)|^2. \tag{7}$$

It has been established both from experiments and from the comparison with S-matrix results that MFF, in general, produces better results than other choices of form factors. Tabulated values of MFF for elements with atomic numbers $1 \leq Z \leq 100$ and momentum transfers $0 \leq x \leq 100\ A^{-1}$ are available [10].

4. Anomalous scattering factors

Form factor is derived with the assumption that the photon energy is large compared with the binding energies of electrons that scatter. Therefore, when photon energy is comparable or

less than the binding energy of the inner electrons, form factors begin to fail. The deviation of form factor from the exact forward scattering amplitude is called the anomalous scattering factor or anomalous dispersion correction. Rayleigh scattering amplitude is a complex quantity, its real part beyond form factor corresponds to dispersion, while its imaginary part corresponds to absorption. Therefore, if a form factor is to characterise the Rayleigh scattering amplitude, it should be

$$f(q) = f_{\mathrm{FF}}(q) + f'(0) + i\, f''(0). \tag{8}$$

Here the forward imaginary part $f''(0)$ is related to the total photo absorption cross section σ_{ph} including bound-bound transitions and bound pair production through the optical theorem

$$f''(0) = \frac{mcE}{2e^2}\,\sigma_{\mathrm{ph}}(E), \tag{9}$$

and the forward real anomalous term is related to $f''(0)$ through the dispersion relation

$$f'(0) = \frac{2}{\pi}\,P\int_0^{\infty}\frac{E' f''(E')}{E'^2 - E^2}\,dE'. \tag{10}$$

Cromer and Liberman [13,14] have published an extensive tabulations of f' and f'' for photon energies corresponding to K_α radiations of Cr, Fe, Cu, Mo and Ag for neutral atoms in the range $3 \le Z \le 98$. Henke *et al* [15,16] tabulated values of anomalous correction terms for elements $1 \le Z \le 94$ for photon energies 100 eV to 2 keV. Both Cromer and Liberman and Henke *et al* used dipole approximations in their estimate of relativistic correction to the high energy limit of forward scattering. It has been realized later that the higher multipoles are also important [17,18]. The correct high energy limit of f' has been obtained using S-matrix calculations and the correction terms defined to be

$$\delta f' = f'(\infty) - f'_{\mathrm{CL}}(\alpha), \tag{11}$$

where CL represents Cromer and Liberman's high energy limit. The correction terms have been tabulated by Kissel and Pratt [19] for all elements in the range $1 \le Z \le 100$. In using Cromer and Liberman's table (incidentally which have been used extensively) one must include the correction term $\delta f'$ as given by

$$f'(0) = f'_{\mathrm{CL}}(0) + \delta f'. \tag{12}$$

It has been demonstrated [20] that the use of correct high energy limit removes the discrepancy between experimental values [21–24]. Figure 2 exhibits comparisons of corrected calculated anomalous scattering factor (f') with measured values for germanium at different photon energies, while Figure 3 exhibits how the agreement with experimental values improve when the correct high energy limit is taken in calculating the anomalous scattering factor (f'). It is to be realized that the dispersion relations relate forward direction

amplitude and not their angle dependence. Some times similar angular dependence as of form factors are used to consider the angular dependence of ASF.

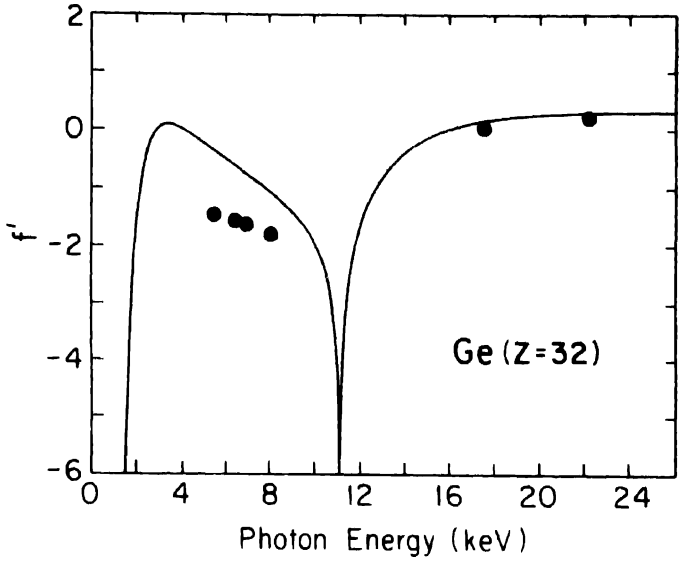


Figure 2. Comparison of experimental values of the real anomalous scattering factors due to Gerward *et al* [22] with theory.

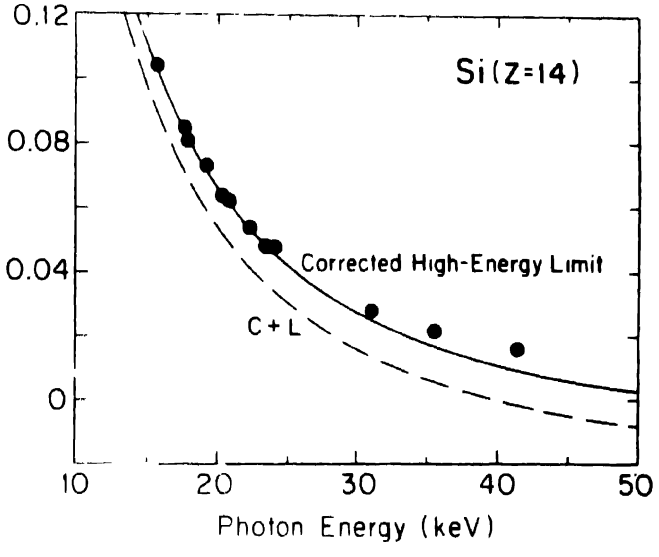


Figure 3. Comparison of experimental values of the real anomalous scattering factors recommended by Deutsch and Hart [21] with theoretical prediction utilizing correct high energy limit values (solid curve) show improved agreement with experiment.

If one uses MFF instead of FF then the corresponding eq. (8) of $f(q)$ will be

$$f(q) = g(q) + g'(0) + ig''(0). \tag{13}$$

Since MFF gives correct high energy limit predictions, g' vanishes in the high energy limit. The anomalous terms g' and g'' are related to the Cromer and Liberman anomalous terms f'_{CL} and f''_{CL} by

$$g'(0) = f'_{CL}(0) - f'_{CL}(\infty) \tag{14}$$

and

$$g''(0) = f''_{CL}(0). \tag{15}$$

5. Comparison of different theories and experiments

We in this section present comparison of Rayleigh scattering cross sections obtained from FF and MFF with and without ASF included with the best available S-matrix results and with experiments to give a general impression of the validity of form factors. Figures 4 and 5

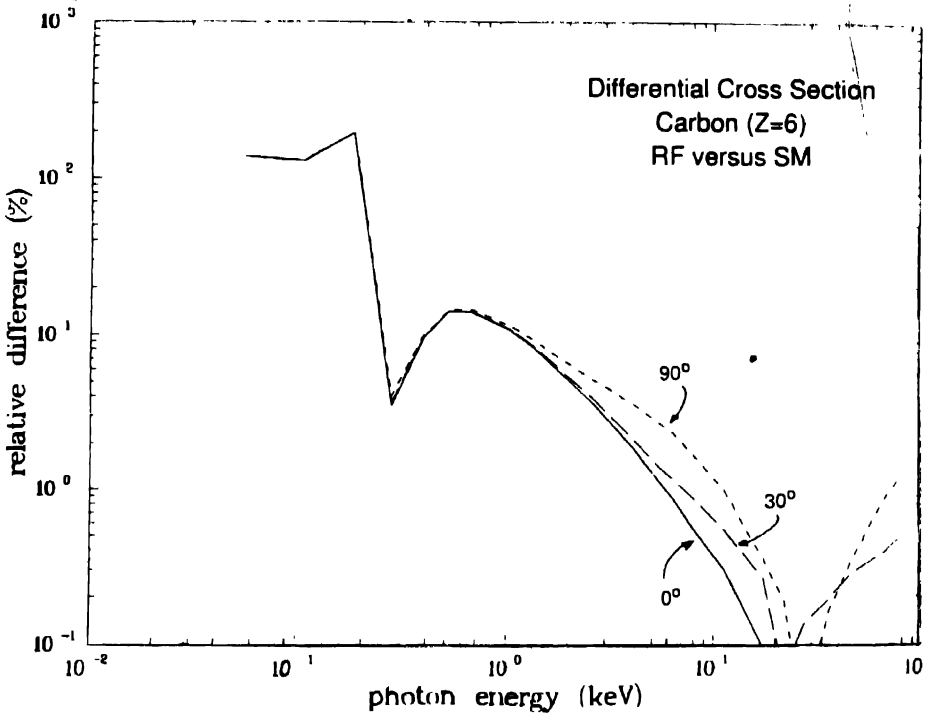


Figure 4. Relative percent differences of Rayleigh scattering cross sections obtained from FF approximation with S-matrix (SM) results for carbon at $\theta = 0°$, 30° and 90°

present the relative percent difference of FF values from the S-matrix results for carbon and lead respectively. It can be seen that for all elements FF approximation gives, in general, good predictions in the forward direction for photon energies well above K-threshold, but it produces extremely poor results for photon energies close and below the K-threshold. With increasing momentum transfer (*i.e.* with increasing angles for a given photon energy or with increasing energy for a given scattering angle) FF starts deviating from the S-matrix results.

It has been observed [25] that differential cross sections obtained in the FF approximation is good (error < 10%) for all angles in light and medium Z elements and for small angles in heavy elements, over a range of photon energies from somewhat above the K-edge to about ten times greater.

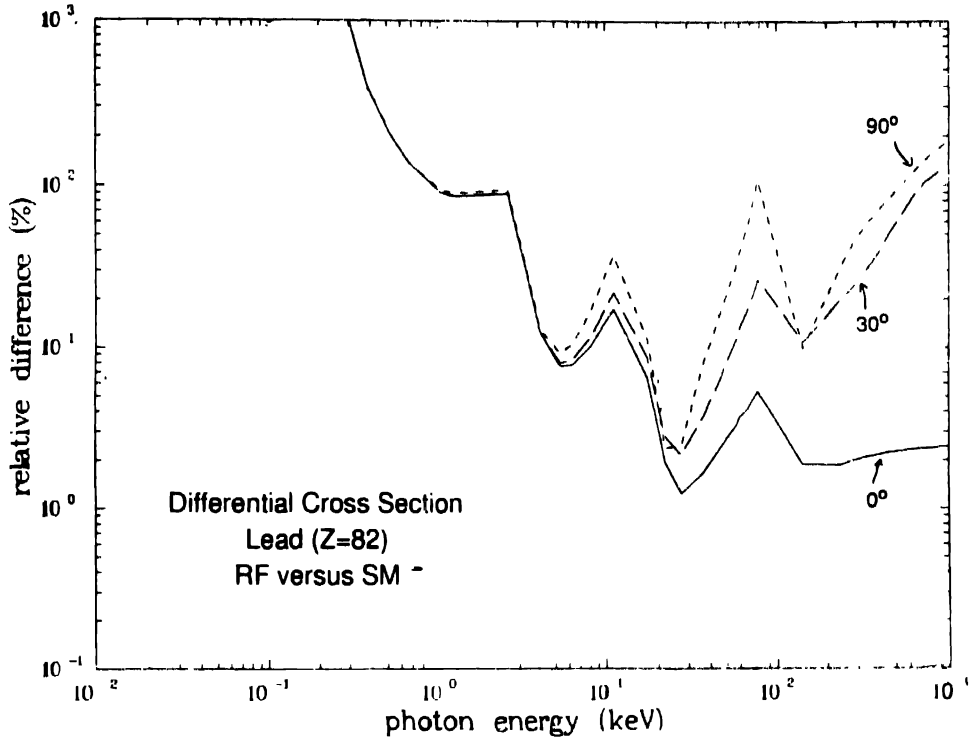


Figure 5. Same as of Figure 4 for lead

Figures 6 and 7 present the relative percent difference of MFF results from the S-matrix results for carbon and lead respectively. It is to be noted that the deviation of MFF from S-matrix calculation, in general, behaves similar to that of FF approximation. Main improvement of MFF, as can be seen, is at forward direction for high photon energies, practically converging with the correct high energy limit.

We present in Figures 8 and 9 the comparison for carbon and lead respectively when ASFs are included with MFF values. Real improvement as can be seen is for photon energies below thresholds. For photon energies below K-threshold, the differential cross section of Rayleigh scattering predicted by MFF + ASF works very well (error < 5%) for all atoms and angles. Above K-thresholds, MF + ASF is very good for the forward direction and small angle scatterings.

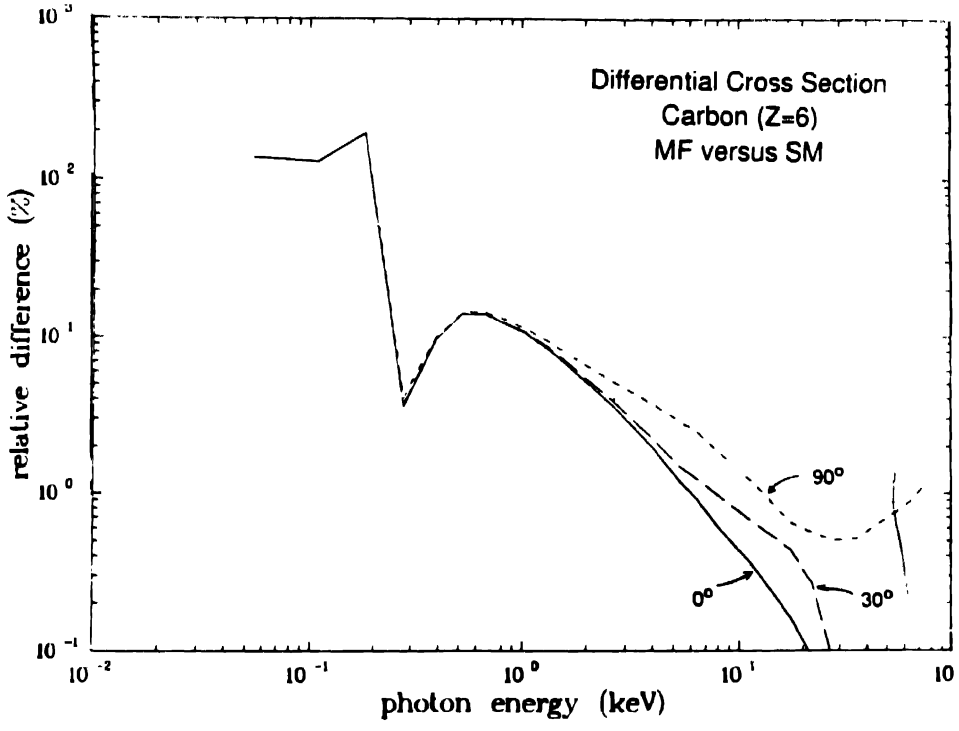
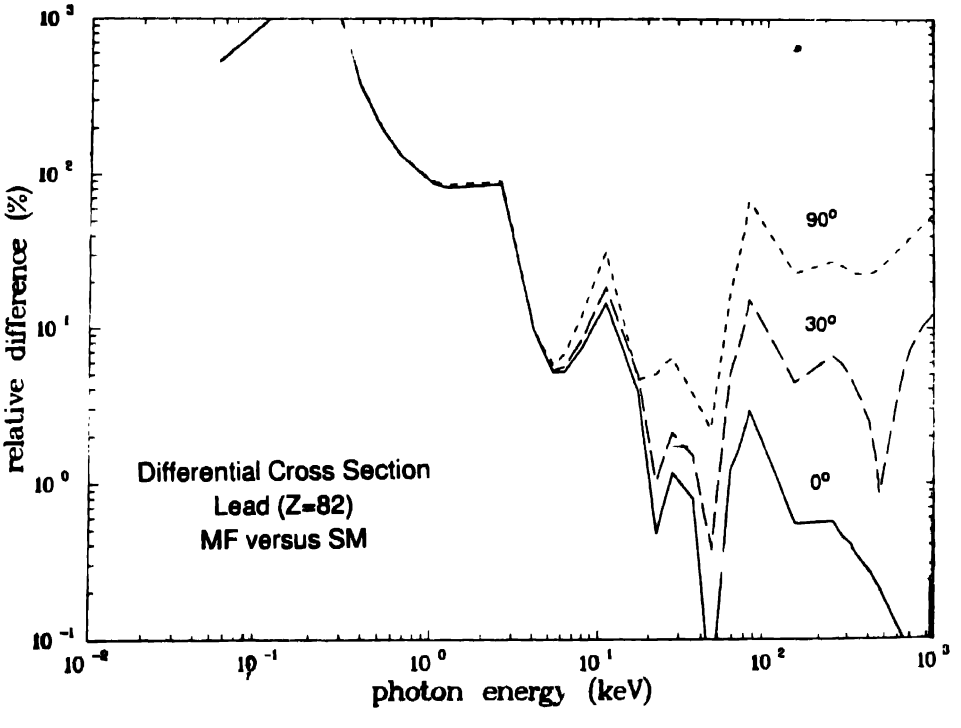


Figure 6. Relative percent differences of Rayleigh scattering cross sections obtained from MFF approximation with S-matrix (SM) results for carbon at $\theta = 0°$, 30° and 90°



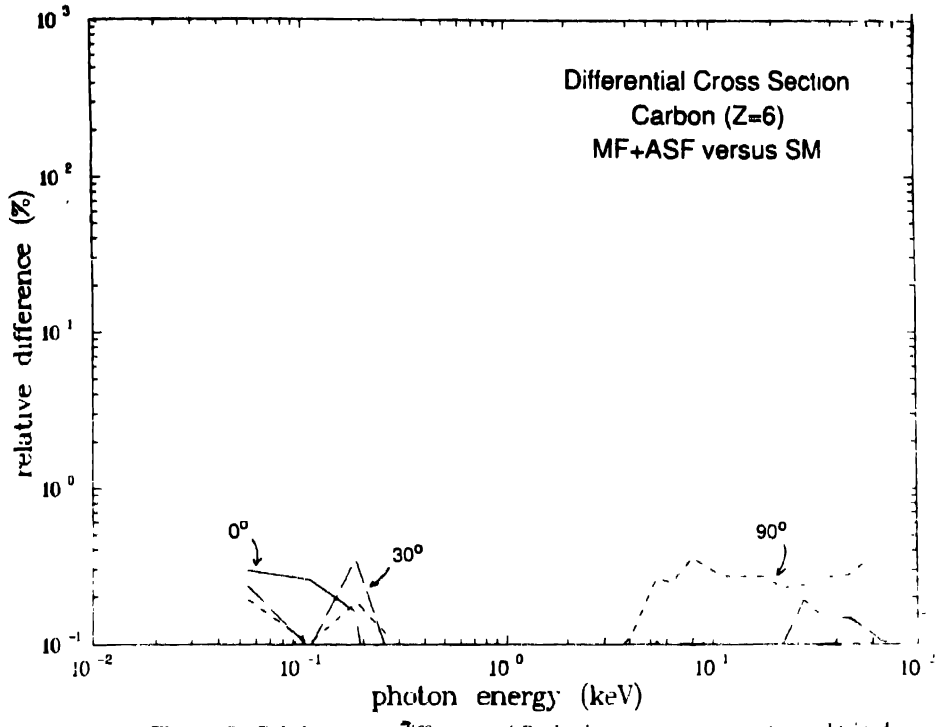
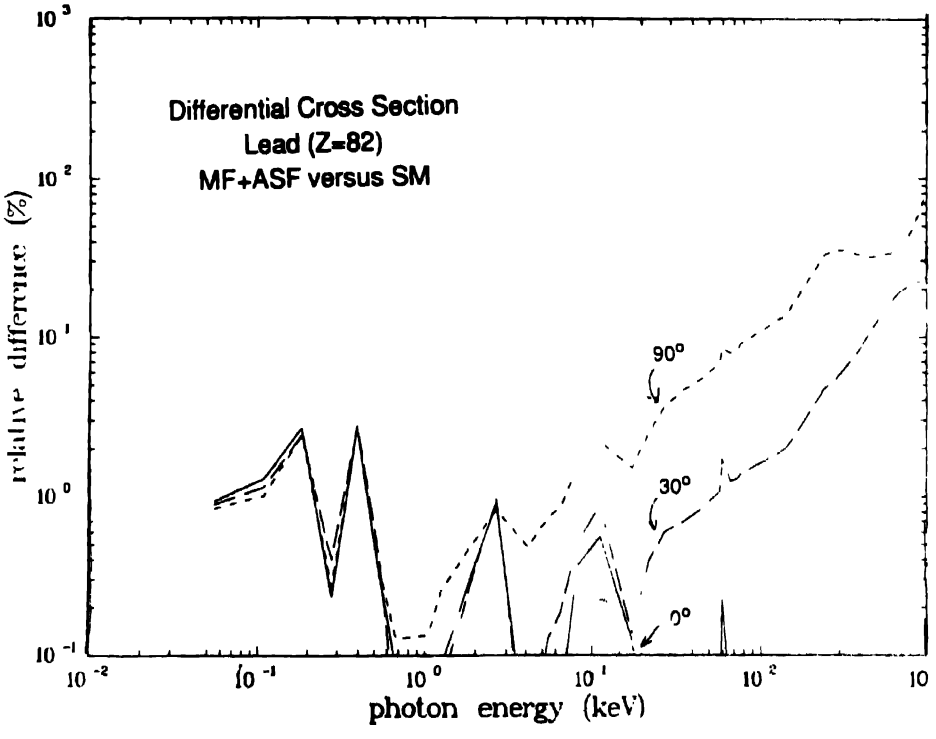


Figure 8. Relative percent differences of Rayleigh scattering cross sections obtained MFF + ASF approximation with S-matrix (SM) results for carbon at $\theta = 0°$, 30° and 90°



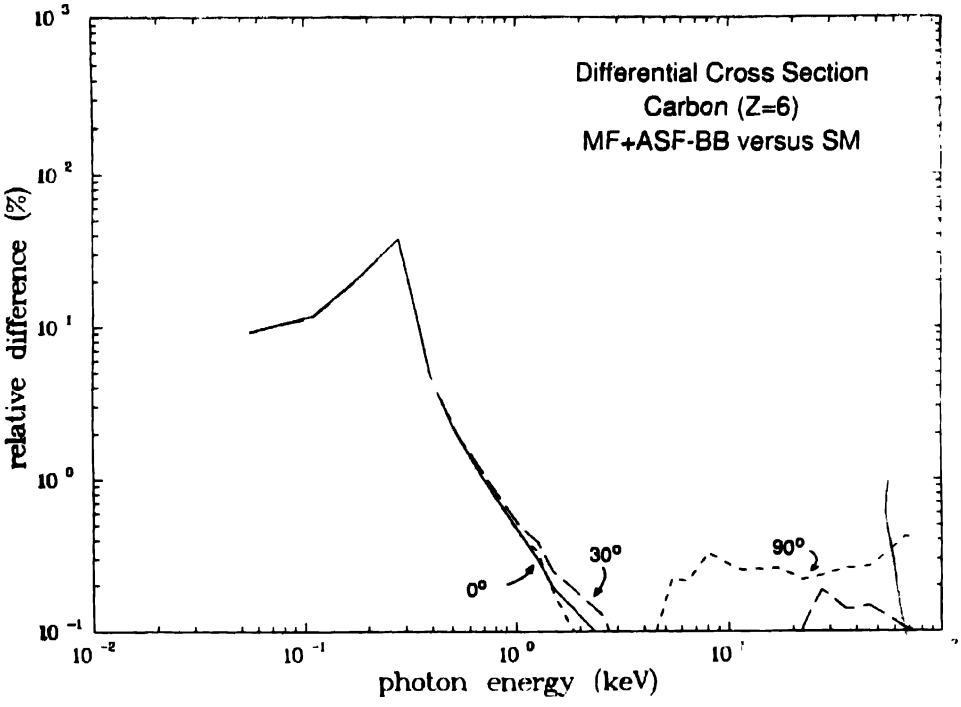


Figure 10. Relative percent differences of Rayleigh scattering cross sections obtained from MFF + ASF – BB (–BB indicates the contributions from bound-bound transitions are taken out) with S-matrix (SM) results for carbon at $\theta = 0°$, 30° and 90°.

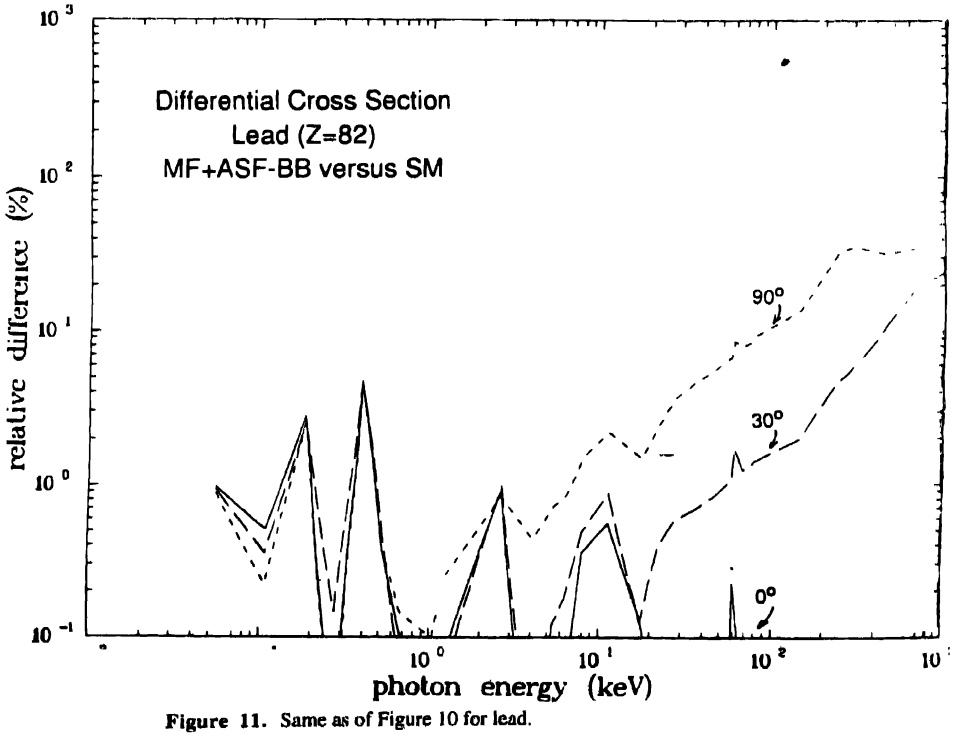


Figure 11. Same as of Figure 10 for lead.

As mentioned earlier, contributions from bound-bound transitions is thought to be small compared to the bound-free transitions and therefore neglected even in many recent computations [26] of ASF. The importance of bound-bound transitions are presented in Figures 10 and 11. As can be understood from the Figures that bound-bound transitions are important for photon energies below K-threshold and more prominent for low Z elements. Comparison of experimental results with different theories for different photon energies and targets are presented in Figures 12–14. As can be seen, MFF with angle independent anomalous scattering factor improves agreement with experiments for all angles and photon

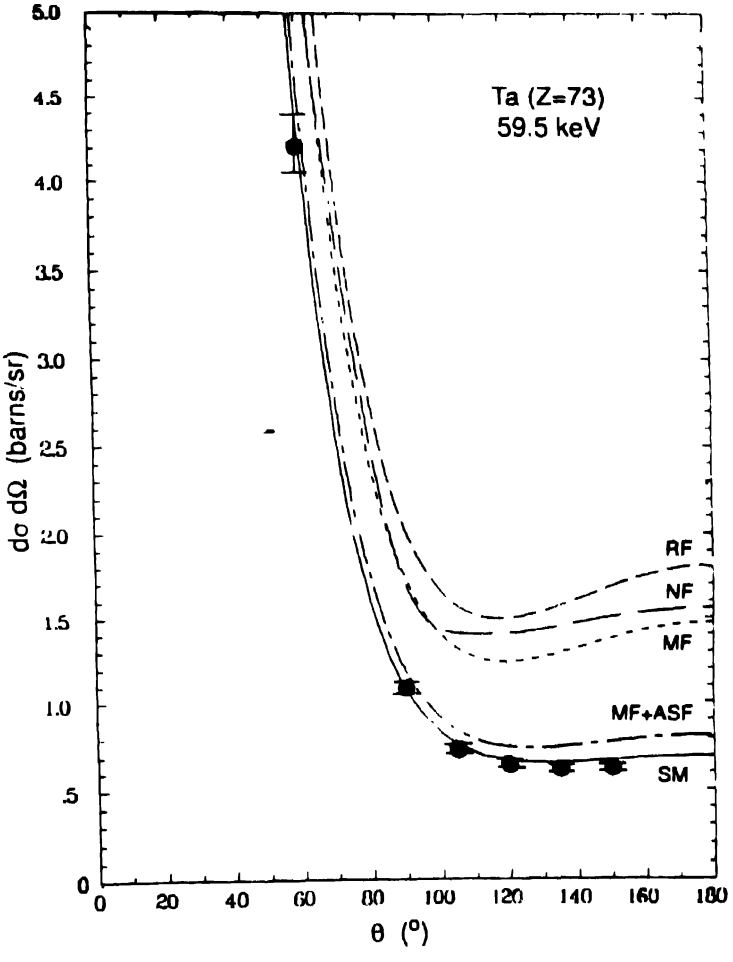


Figure 12. Comparison of experimental results with S-matrix and different form factors for Ta at 59.5 keV. NF– nonrelativistic form factor, RF– relativistic form factor, MF– modified form factor and MF + ASF– modified form factor with anomalous scattering factors.

energies near and below K-threshold, while predicted values using S-matrix agree quite well with experimental results. Deviations of experimental results from the values predicted using

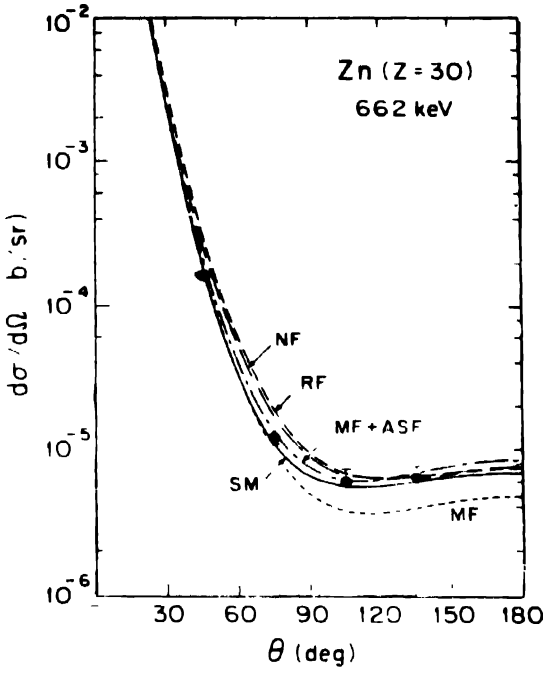


Figure 13. Comparison of experimental results with S-matrix and different form factors for Zn at 662 keV. NF– nonrelativistic form factor, RF– relativistic form factor, MF– modified form factor and MF + ASF– modified form factor with anomalous scattering factors.

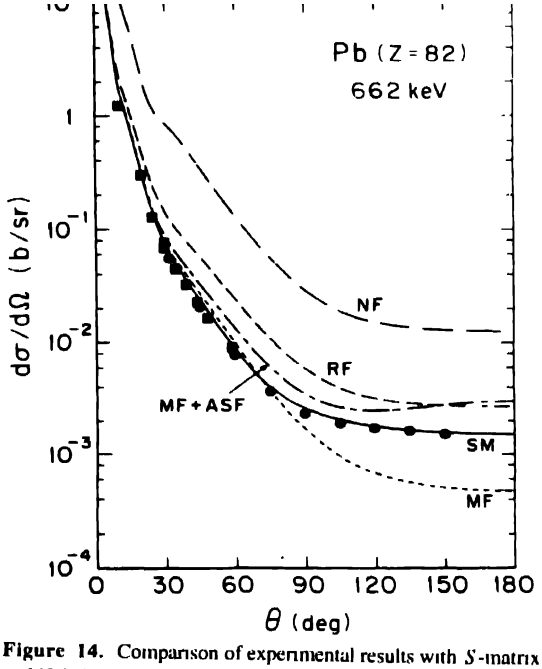


Figure 14. Comparison of experimental results with S-matrix and different form factors for Pb at 662 keV. NF– nonrelativistic form factor, RF– relativistic form factor, MF– modified form factor and MF + ASF– modified form factor with anomalous scattering factors.

MFF plus angle independent ASF at large momentum transfer indicate that the assumption of angle independence ASF is not valid for back angles.

6. Conclusions

Our systematic assessment of FF, MFF and ASF approximations and their validity in respect to second order S-matrix results and experiments show that FF and MFF, in general, provide good predictions of small angle differential cross sections for photon energies above K-threshold. They fail at all angles for photon energies below K-threshold and at large angles for photon energies well above K-threshold. Use of MFF with angle independent ASF agrees with the S-matrix results within five percent for all angles and all atoms, for photon energies below K-threshold, while for finite angles of photon energies well above K-threshold angle dependence of ASF should be introduced.

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